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Efficient planar perovskite solar cells based on low-cost spin-coated ultrathin Nb_2O_5 films

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ABSTRACT

In planar perovskite solar cells (PSCs), the electron transport layer (ETL), with the function of transporting electrons and blocking holes, plays a significant role in determining the photoelectric conversion properties. Thus, it is crucial to exploit potential ETL materials for improved performance. Herein, we demonstrate efficient planar PSCs employing ultrathin Nb_2O_5 films as ETLs fabricated by a facile spin-coating method. The effects of the precursor concentration and annealing time of Nb_2O_5 on the photovoltaic performance are investigated in detail. The planar PSCs constructed with 0.02 M-prepared Nb_2O_5 films sintered for 1 h possess an optimized performance, giving rise to a champion efficiency of 14.82% with high reproducibility. The superior performance is ascribed to the appropriate conduction band position of Nb_2O_5, high transmittance, increased charge transport, and diminished charge recombination of the Nb_2O_5 film. The results demonstrate that the utilization of spin-coated Nb_2O_5 as the ETL provides a new platform to construct highly-efficient planar PSCs.

1. Introduction

Over the last few years, organic-inorganic hybrid lead halide perovskites have emerged as promising materials for photovoltaic application, owing to their unique properties, including large absorption coefficient, long charge diffusion length, high carrier mobility, and simple production process (Lee et al., 2012; Xing et al., 2013; Wehrenfennig et al., 2014). Since the first utilization of perovskite as sensitizer in dye-sensitized solar cells (Kojima et al., 2009), extensive efforts have been focused on perovskite solar cells (PSCs). The power conversion efficiency (PCE) of PSCs has boosted from 3.8% to over 22.1% in a short few years (Zhao and Zhu, 2016). There are two major configurations for PSCs: mesoscopic and planar architectures. The planar devices have attracted wide interests because of the simple structure and ease in fabrication process (Mei et al., 2014; Liu et al., 2013). The conventional planar PSCs are composed of fluorine-doped tin oxide (FTO) used as the anode, an electron transport layer (ETL), a perovskite layer as light-absorbing material, a hole transport layer (HTL), and metal materials (Au or Ag) as the cathode. The ETL plays an important role in extracting and transporting photogenerated electrons from perovskite absorber to the FTO meanwhile blocking holes generated in the perovskite, serving as an electron-selective and hole-blocking layer (Wu et al., 2017). To obtain highly-efficient perovskite solar cells, a thin, transparent and electrically conductive ETL without pinholes is crucial.

Currently, the most commonly used ETL material in PSCs reported in literatures is TiO_2, owing to its high stability, innate transparency, low cost, and appropriate conduction band (CB) level matching with perovskite layers, leading to fast electron injection from perovskite to TiO_2 layers (Haque et al., 2017). A large variety of techniques have been developed to fabricate TiO_2 layer, such as spin-coating, magnetron sputtering, and spray pyrolysis (Seo et al., 2016; Yang et al., 2015; Heo et al., 2016). However, TiO_2 was reported to have intrinsic low electron mobility and poor charge transport property, resulting in high electron-hole recombination that hinders the enhancement of PCE in PSCs. Thus, a large number of investigations have been made to alleviate this problem (Heo et al., 2015; Ma et al., 2016; Zhang et al., 2016; Li et al., 2017). Modification of TiO_2 has been demonstrated to be an effective approach to improve the photovoltaic performance of PSCs. For instance, metal ions were doped to modify TiO_2 ETL. Liu et al. (2017) adopted Li-doped TiO_2 as ETL in PSCs, which exhibited superior electron transport property by reducing electronic trap states, resulting in improved PCE from 14.2% to 17.1% with negligible hysteresis. Zhou et al. (2014) employed Y-doped TiO_2 as an efficient ETL for PSCs with efficiency up to 19.3%, resulting from improved charge extraction and injection abilities. Apart from TiO_2, other semiconductor materials with appropriate band energy level and excellent electron mobility feature were developed and demonstrated to be alternative ETL materials, such

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as SnO_2, ZnO, and CdS (Anaraki et al., 2016; Tseng et al., 2016; Liu et al., 2015). For example, Anaraki et al. (2016) employed SnO_2 as the ETL, resulting in a V_{oc} higher than 1.2 V, and finally achieved a high PCE over 20%. Exceeding 17% PCE of PSCs based on ZnO ETLs was achieved by Tseng et al. (2016). Accordingly, it is essential to develop promising ETL materials and further enhance the photovoltaic performance.

As a transparent, highly stable, and water-insoluble metal oxide, Nb_2O_5 (an n-type semiconductor with a band gap of about 3.4 eV) has been widely utilized in photocatalysts, gas sensors, supercapacitors, and dye-sensitized solar cells (Guo et al., 2014; Kadir et al., 2015; Lim et al., 2015; Kim and Moon, 2012). Considering its high electron mobility and suitable CB level, Nb_2O_5 is one of the most promising candidates as the ETL in PSCs. However, only several studies have been done on the application of Nb_2O_5 in PSCs. Kogo et al. (2015) reported the application of Nb_2O_5 ETL in perovskite solar cells using Al_2O_3 as the mesoporous scaffold layer, attaining a lower efficiency than traditional TiO_2 mesoporous PSCs. Fernandes et al. (2016) applied Nb_2O_5 ETL in mesoscopic PSCs and demonstrated PCE of 12.3%, with TiO_2 as scaffold layer. Noted that the two above-mentioned PSCs were mesoscopic architectures based on the mesoporous scaffold layer, which could not completely replace TiO_2. Moreover, their PCEs are far from satisfaction. Recently, Feng et al. (2017) applied e-beam evaporated Nb_2O_5 ETL to construct large-area flexible perovskite solar cells with efficiency up to 15.56%. Ling et al. (2017) demonstrated the application of radio frequency magnetron sputtered amorphous Nb_2O_5 as ETL on flexible PSCs, and attained an optimal PCE of 12.1%. In spite of the respectful photovoltaic performance, their fabrication process usually requires sophisticated instruments and strictly-controlled environment. Thus, it is desirable to develop facile solution-processed approach to fabricate Nb_2O_5 ETL so as to simply the fabrication process and lower cost.

In this work, we for the first time develop the spin-coated ultrathin Nb_2O_5 film as an ETL for efficient planar PSCs. The effects of precursor concentration and annealing time of Nb_2O_5 on the PSC performance has been systematically illustrated. The results demonstrate that the suitable conduction band position of Nb_2O_5 ETL, high transmittance, increased charge transport, and diminished charge recombination account for the enhancement in the short circuit current density (J_{sc}) and open-circuit voltages (V_{oc}), eventually yielding a champion PCE of 14.82% and an average efficiency of 13.95 ± 0.54%.

2. Experimental

2.1. Materials and preparation

FTO glass substrates were obtained from Yingkou Opvtech New Energy CO., Ltd. Methylammonium iodide (CH_3NH_3I) and 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′- spirobifluorene (spiro-OMeTAD) were obtained from Xi'an Polymer Light Technology Corp. Niobium (V) chloride ($NbCl_5$, 99.9%), Lithiumbis-(trifluoromethylsulphonyl)imide (Li-TFSI) and 4-tert-butylpyridine (TBP) were purchased from Aldrich. Acetylacetonate (99%) was purchased from SCRC. Ethanol absolute (99.5%), Lead (II) chloride ($PbCl_2$, 99%), and N, N-dimethylformamide (DMF, 99.9%) were bought from Alfa. Unless specified, all the chemicals were used directly without further purification. The FTO substrates were ultrasonically cleaned with acetone, ethanol, and deionized water sequentially for 20 min. Before the fabrication of solar cells, the cleaned FTO substrates were then treated with Ultraviolet Ozone for 15 min.

2.2. Preparation of ultrathin Nb_2O_5 films

Various concentrations of Nb_2O_5 precursor solutions were prepared by dissolving niobium (V) chloride with various mole fraction (0.01, 0.02, 0.04, and 0.06 M, respectively) in anhydrous ethanol overnight. The ultrathin Nb_2O_5 films were prepared by spin-coating the prepared precursor solutions on cleaned FTO substrates at 3000 rpm for 30 s and sintered at 500 °C for 1 h in air.

2.3. Fabrication of solar cells

The above prepared Nb_2O_5 films were used as the ETLs. The perovskite layer was prepared by spin-coating precursor solution of $CH_3NH_3PbI_{3-x}Cl_x$ onto the Nb_2O_5 substrate at 3000 rpm for 40 s. Then the film was annealed at 105 °C for 1 h to form crystalline perovskite layer. The $CH_3NH_3PbI_{3-x}Cl_x$ precursor was synthesized by dissolving CH_3NH_3I and $PbCl_2$ (3: 1 M ratio, 40 wt%) in DMF at 60 °C for 12 h. The HTL solution (spiro-OMeTAD, 25 μL) was deposited on the perovskite layer by spin-coating at 2000 rpm for 45 s. The spiro-OMeTAD precursor solution was made by dissolving 72.3 mg of spiro-OMeTAD, 17.5 μL of 520 mg mL^{-1} lithiumbis-(trifluoromethanesulfonyl)imide (LiTFSI) in acetonitrile, and 28.8 μL of 4-tert-butylpyridine (TBP) in 1 mL of chlorobenzene. Finally, a silver counter electrode (100 nm-thick) was deposited by thermal evaporation with a shadow mask on the top of devices. The active area of the final device is 0.15 cm^2.

2.4. Characterization

The surface morphology, cross-section, and elemental mapping of the samples were measured by a field-emission scanning electron microscope (FE-SEM, Hitachi, SU8010) with energy dispersive X-ray (EDX) spectrometer. The phase of the sample was characterized by an X-ray diffractometer (XRD) (D/MAX-III-B-40KV, Cu Kα radiation, λ = 0.15418 nm). X-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) were carried out using a XPS/UPS system (Thermo Scientific, Escalab, 250Xi). The current-voltage (*J-V*) and external quantum efficiency (EQE) were tested with a Newport solar simulator under AM 1.5G irradiation (100 mW cm^{-2}) in air without encapsulation. All devices were measured in air with temperature of 25 °C and humidity of 40%. The absorbance and transmittance spectra were recorded on a UV–vis spectrophotometer (Shimadzu, UV-3600). The photoluminescence (PL) spectrum was detected with a spectrofluorometer (Horiba, Fluoromax-4) with a 525 nm excitation wavelength at room temperature. The electrochemical impedance spectroscopy (EIS) was measured with an electrochemical workstation (Autolab, PGSTAT 302 N) under the light condition at zero-bias voltages with an alternative signal amplitude of 5 mV and in the frequency range of 400 kHz–0.01 kHz.

3. Results and discussion

Fig. 1 presents the top-view SEM images of pure FTO glass (Fig. 1a) and spin-coated Nb_2O_5 films prepared from precursor solutions of 0.01 M, 0.02 M, 0.04 M, and 0.06 M (Fig. 1b–e), respectively. The insets are the enlarged SEM images. As seen, FTO substrate is composed of large crystals with smooth exposed surface. After spin-coating of Nb_2O_5 films with different precursor concentrations from 0.01 M to 0.04 M on the FTO substrate, the resulting films almost remain the same surface morphology with bare FTO glass. For the Nb_2O_5 film prepared with 0.01 M precursor solution, it is observed that the FTO glass cannot be covered completely, which would result in the direct contact of the perovskite layer with FTO substrate and produce short circuit. With the increase of precursor concentration, the distribution of Nb_2O_5 particles on the FTO substrates becomes denser, exhibiting full coverage on the surface. This indicates the formation of transparent, homogeneous and ultrathin Nb_2O_5 films. When 0.06 M Nb_2O_5 precursor was used, abundant of defects and cracks appear on the Nb_2O_5 film, representing a fragmentary and irregular surface morphology, as illustrated in Fig. 1e. The defective and rough surface leads to uneven coverage of the following perovskite layer, which would bring retarded electron transmission and high charge recombination. Fig. 1f presents the typical elemental mapping of the spin-coated Nb_2O_5 film prepared from 0.02 M